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KINETICS OF THE DISORDER→ORDER TRANSFORMATION IN THE Cu – 47 at.% Pd ALLOY

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On the basis of experimental data obtained with the help of resistometric measurements, kinetic C-curves of the isothermal disorder→order transformation have been constructed and the activation energy of the atomic ordering process in the quenched Cu – *47 at.%* Pd *alloy has been calculated. Deviations from the data in the literature are explained by differences in the methods of obtaining the initial disordered state of the alloy.*

Keywords: atomic ordering, kinetics of phase transformations, resistometric measurements.

INTRODUCTION

Cu–Pd alloys, containing from 36 to 48 at.% Pd, at temperatures below 600°C undergo a structural $A1 \rightarrow B2$ phase transition in the process of which the disordered HCC lattice is restructured as a FCC ordered lattice [1]. An interesting property of these alloys is the fact that the maximum temperature and rate of atomic ordering is demonstrated by the alloy containing 40 at.% Pd. For this reason, in the study of the Cu–Pd system greatest interest has been focused on the compositions at or near Cu – 40 at.% Pd. A detailed analysis of the properties of structural transformations in this alloy during the course of the order – disorder transformation, together with a large number of references to the results of other researchers, was published, for example, in [2].

Recently, interest has gradually shifted toward Cu–Pd alloys with higher palladium content. For example, the Cu – 47 at.% Pd alloy in the ordered state has a low electrical resistivity ($\rho = 4.0 \cdot 10^{-8}$ Ω·m [3]), which fact can be used in instrument making to fabricate conductors of weak electrical signals. In addition, its peculiar chemical properties make it promising as a catalyst [4] or material for selective membranes for extracting hydrogen from gaseous mixtures [5]. Thus, a study of the properties of the order – disorder phase transformation, and also the structure and properties of Cu–Pd alloys near the equiatomic composition, is of both scientific and practical interest.

The resistometric method is an express and relatively simple means of investigating phase transformations, and it allows one with sufficient accuracy to determine the temperature intervals of structural transformations and to estimate the ratio of new phase to the matrix. The use of this method to study order – disorder transitions is facilitated by the fact that the onset of atomic order, as a rule, is accompanied by a substantial increase in the electrical conductivity of the material. For example, the electrical resistivity of Cu–Pd alloys in the disordered and ordered states differs by a factor of several times [3, 6].

The aim of the present work is to examine the kinetics of atomic ordering of the Cu – 47 at.% Pd alloy with the help of resistometric measurements.

MATERIAL AND EXPERIMENTAL TECHNIQUE

The alloy sample was smelted from copper and palladium of 99.98% purity. Smelting was carried out in vacuum not worse than 10^{-2} Pa followed by casting into a graphite crucible. An ingot with diameter 5 mm was

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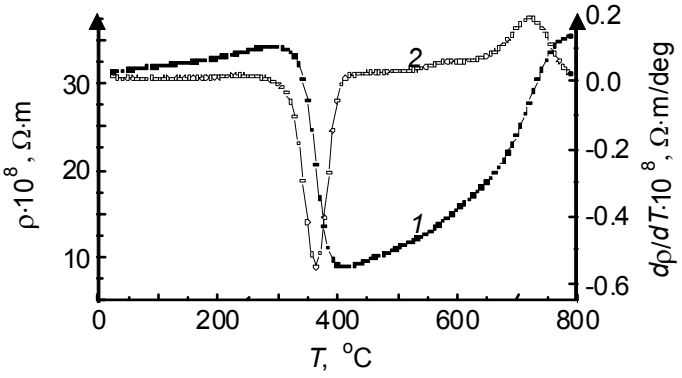

Fig. 1. Dependence of the electrical resistivity (curve *1*) and the corresponding temperature derivative (curve *2*) of a sample of the quenched Cu – 47 at.% Pd alloy for a heating rate of 120 deg/h.

homogenized at a temperature of 850°C for 3 hours with subsequent quenching in water. The metal rework was realized by alternation of wire-drawing to 75% and recrystallization annealing at 850°C for 1 hour with subsequent cooling in water.

The main technique employed in the present work was resistometric measurements by the four-pole method. Recording of all necessary parameters (temperature of oven and of sample, and also the voltage drop on the sample) was realized with the help of a data acquisition and analysis system constructed from ADAM-4000 modules and the SCADA-system Advantech GeniDAQ. A more detailed description of the experimental setup can be found in Reference [7].

The sample for these measurements consisted of a wire 0.22 mm in diameter and 120–140 mm in length, and the constant current feed stood at 10 mA. Note that the onset of atomic long-range order causes a lowering of the electrical resistivity of the alloy by a factor of 6, which makes it possible to determine the quantitative ratio of phases during the disorder – order transformations with a fairly high degree of accuracy.

The measurements were performed on samples placed in a vacuum-sealed quartz ampoule or immersed in a melt bath with a mixture of potassium and sodium nitrate. Isothermal annealing as well as continuous heating at a rate of 120 deg/h were performed. The temperature during isothermal annealings varied by only ±2°.

To calculate the activation energy of the phase transformation from the resistometric measurements, we used the technique described in Reference [8].

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 displays the dependence of the electrical resistivity of the quenched Cu – 47 at.% Pd sample (curve *1*) and the corresponding temperature derivative (curve *2*), obtained for a heating rate of 120 deg/h.

The initial state of the alloy was formed by quenching from 850°C. The electrical resistivity of the quenched alloy at room temperature is $\rho = 31.6 \cdot 10^{-8}$ Ω·m, upon heating it varies by several-fold (curve *1* in Fig. 1). At first, in the temperature interval from 270 to 420°C the electrical resistivity is observed to fall sharply, which is caused by processes of atomic ordering. The maximum rate of the order→disorder phase transformation under the given experimental conditions occurs at 365°C, which can be clearly seen from the minimum in the graph of the derivative $d\rho/dT$ (curve *2* in Fig. 1). Upon further heating, up to 530°C, the alloy is found in the ordered state, the electrical resistivity of the sample in this range is quite low, and its moderate growth is governed by the non-zero temperature coefficient of the electrical resistivity. Further increase in the temperature (all the way to the end of the experiment at 780°C) leads to a gradual disordering of the sample, which is manifested by the growth of its electrical resistivity. In this regard, it is clear from the graph of the temperature derivative that the process of the $B2 \rightarrow A1$ phase transformation is realized, as it

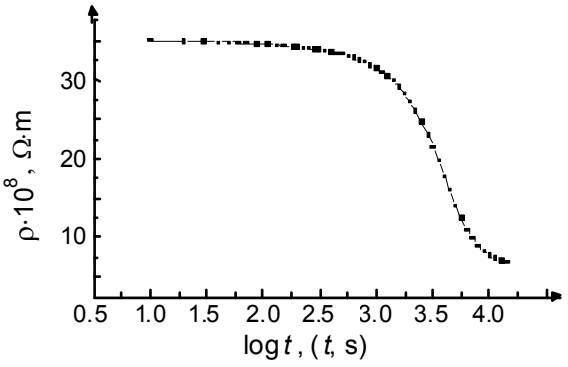

Fig. 2. Dependence of the electrical resistivity of the Cu – 47 at.% Pd alloy on holding time in a salt bath at 347°C.

were, in two steps: at first, a slight hump is observed at 570°C; then a second peak, of significantly greater intensity, is observed at 715°C. Note that according to the phase diagram [1], at temperatures above 580°C the investigated sample should be found in the disordered state.

In the literature, attention has been drawn more than once to the possibility of the existence of several stages in the disordering of Cu–Pd alloys. Moreover, Klopotov et al. [10] constructed temperature-time curves (*C*-curves), describing the order→disorder phase transformation in the Cu – 39.5 at.% Pd alloy, which have two maxima of the rate of this process in different temperature intervals.

However, upon examination of the formation of atomic order, no stages of the $A1 \rightarrow B2$ transformation in Cu–Pd alloys were observed. For example, in the construction of diagrams of isothermal ordering kinetics in Cu–Pd alloys in [12] (with palladium content from 44 to 48 at.%) no peculiarities were noted. At the same time, upon acquainting ourselves with the results of this work, questions arose regarding experimental technique: quenching of the sample *to the disordered state* was realized by air-cooling while heat treatment was carried out by placing the vacuum-sealed ampoule containing the samples in a muffle furnace.

As was shown earlier in the example of the Cu– 40 at.% Pd alloy [13], in the case when the rate of atomic ordering is large, methodical inaccuracies during quenching and subsequent annealing can lead to a distortion of the true transformation pattern. Indeed, for relatively slow heating the ordering process can occupy a noticeable volume of the alloy up to the moment when the prescribed temperature of the experiment is reached, which becomes in the final analysis the obvious reason for obtaining incorrect results. The quenching rate plays a substantial role: as is well known, for cooling in air, ordering nuclei have time to form in Cu–Pd alloys. Thus, for a high ordering rate, in the construction of the temperature-time curves of the phase transitions, one should use only very fast heating rates (for example, Volkov [15] proposed immersing the Cu – 40 at.% Pd samples in a salt melt).

For the above-indicated reasons, in the present work the disordered state in the samples was fixed by quenching in water with concomitant breakage of the ampoule (a graph of the temperature dependence of the electrical resistivity of the alloy in this state is shown in Fig. 1). To construct the temperature-time curves of the $A1 \rightarrow B2$ phase transformation in Cu – 47 at.% Pd, we measured the dependence of the electrical resistivity of the initially quenched samples on the holding time in salt melts at various temperatures. As an example, Figure 2 displays an experimental curve of the variation of the electrical resistivity of a sample placed in a salt bath at 347°C.

As can be seen from Fig. 2, after some incubation period the electrical resistivity of the quenched sample begins to gradually decrease, which indicates the onset of the disorder→order phase transformation. The process finishes up after 4.5 h, during which time complete ordering of the material takes place and, as a result, the electrical resistivity falls to a minimum and becomes constant.

Experiments measuring the dependence of the electrical resistivity on holding time were performed at the temperatures 347, 375, 389, 413, 428, 449, 461, and 474°C. The choice of temperatures was occasioned by the

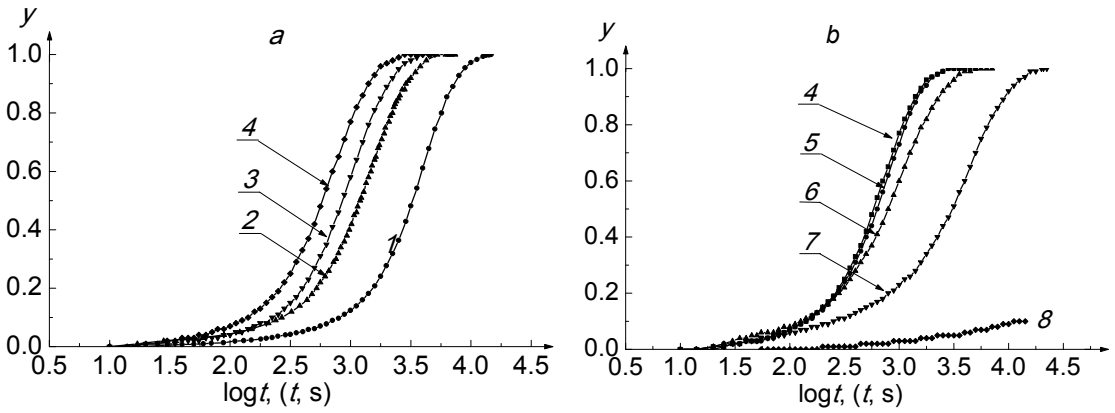

Fig. 3. Dependence of the degree of ordering on holding time: *a*) at temperatures 347 (curve *1*), 375 (curve *2*), 389 (curve *3*), and 413°C (curve *4*); *b*) at temperatures 413 (curve *4*), 428 (curve *5*), 449 (curve *6*), 461 (curve *7*), and 474°C (curve *8*).

impossibility of exactly adjusting the salt bath to one or another regime. Each experiment, as a rule, lasted about 10 h, of which from 4 to 5 h were needed to stabilize the temperature of the salt bath.

From the dependences obtained, we can calculate the degree of transformation (y) from formula (1) for the transition of the disordered state of the alloy to the ordered state as a function of annealing time at one or another temperature:

$$y = \frac{\rho_1 - \rho_t}{\rho_1 - \rho_2}, \tag{1}$$

where ρ_1, ρ_2 are the resistivities of the initial disordered alloy and the completely ordered alloy, respectively, and ρ_t is the current value of the electrical resistivity.

The calculated results shown in Fig. 3 display the variation of the content of $B2$ phase (y) as a function of the logarithm of holding time of the quenched Cu – 47 at.% Pd samples at different temperatures. From Fig. 3*a* it can be seen that for these annealing temperatures starting at 347°C (curve *1*) the transition from the disordered state to the ordered state is completed sequentially faster with each step up in annealing temperature. The highest reaction rate is observed at 413°C (curve *4*). With further increase in the temperature the rate of ordering slows down (Fig. 3*b*).

The maximum heat treatment temperature in this study was 474°C; however, at this temperature the rate of phase transformation had dropped so low that after holding for a duration of 5 h, less than 15% ordered phase had formed (curve *8* in Fig. 3*b*). Because of limitations in annealing time, it was not possible to study the kinetics of ordering of the Cu – 47 at.% Pd alloy at this or higher temperatures.

On the basis of the obtained data we can construct isothermal transformation diagrams, which it is customary to call *C*-curves, but in foreign articles they are often referred to as *TTT*-diagrams (Temperature–Time–Transformation). Such a diagram shows the relation between temperature T (in linear scale) and the time t (in logarithmic scale) needed to reach a predetermined degree of transformation. Thus, the entire diagram of isothermal transformation consists of a set of *C*-curves describing the dependence $T = f(\log t_y)$, where t_y is the time needed to reach the degree of transformation y.

Figure 4 presents diagrams of the kinetics of isothermal ordering of the Cu – 47 at.% Pd alloy. The graphs were constructed for the degrees of transformation 20, 40, 60, 80, and 100%.

The results presented in Fig. 4 differ substantially from the diagrams published in [12]. Since the Cu – 47 at.% Pd alloy was not studied in [12], a comparison is made here with the *C*-curves for the Cu – 46 at.% Pd and Cu – 48 at.% Pd alloys. It turns out that in Reference [12] formation of the completely ordered state in both alloys is completed significantly faster while the indicated temperature of maximum transformation rate is lower than in Fig. 4.

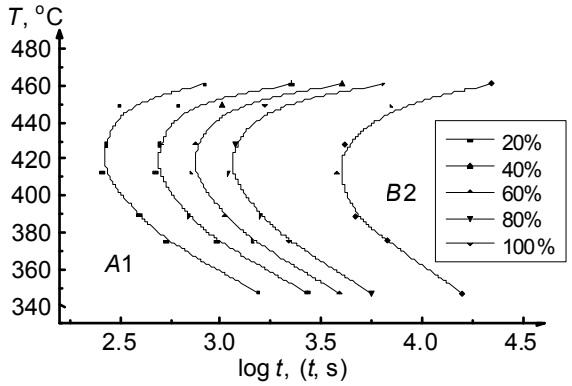

Fig. 4. Diagrams of the kinetics of isothermal ordering of the initially quenched Cu – 47 at.% Pd alloy.

This confirms that the sample preparation technique chosen in Reference [12] was not sufficiently thought out, and as a result the samples in the initial state contained some amount of nuclei of the ordered phase. Hence it follows that the estimates of the activation energy of the ordering process in Cu–Pd alloys in Reference [12] are in need of correction.

On the basis of the above results (Figs. 3 and 4) we estimated the activation energy of ordering in the quenched Cu – 47 at.% Pd alloy.

The relation between the degree of transformation of the quenched alloy into an ordered solid solution and the annealing time can be expressed by the Avrami equation (in foreign works this equation is called the Johnson–Mehl–Avrami equation) [8]

$$y = 1 - \exp\left[-(k \cdot t)^n\right], \tag{2}$$

where n is a power associated with the transformation mechanism, k is the transformation rate constant at the given temperature, and t is the transformation time. For the majority of transformations the power n does not depend on temperature over a wide temperature interval. Since its value is determined by geometric factors of the process, n will vary only when they are varied. On the contrary, the coefficient k varies markedly with temperature [16].

Taking the double logarithm of Eq. (2) leads to the relation

$$\ln\ln\left(\frac{1}{1-y}\right) = n \cdot \ln t + n \cdot \ln k\,. \tag{3}$$

The magnitudes of n and k can be determined from the slope and the y-intercept of the graph of the dependence of $\ln\ln[1/(1-y)]$ on $\ln t$, respectively (Fig. 5).

The calculations performed with the help of Fig. 5 show that in the process of the structural-phase transformations the values of the parameters n and k vary strongly with increasing temperature. It is known [16] that to conserve the mechanism of transformation the value of n must remain constant (in this case the curves in Fig. 5 would be parallel). As can be seen from Fig. 5, in the given case the parameter $n \approx 1.4$ in the temperature region 347–428°C and with increasing temperature falls to values less than 1.0 (Fig. 6).

According to [16] the parameter n takes values around 1.5 for diffusion-controlled growth of spheroids of arbitrary shape and $n \approx 1$ for long cylinders (rods) growing along their radii. From the obtained data we can conclude that with increasing temperature the mechanism of formation of an ordered structure varies with increasing temperature. Klopotov et al. [17] came to a similar conclusion on the basis of electron-microscope observations. Upon cooling of the Cu – 39.5 at.% Pd alloy from a temperature above critical, Klopotov et al. [17] recorded a precipitation of the ordered phase in the form of two morphological components: they observed interlayers along the grains boundaries and lamellar

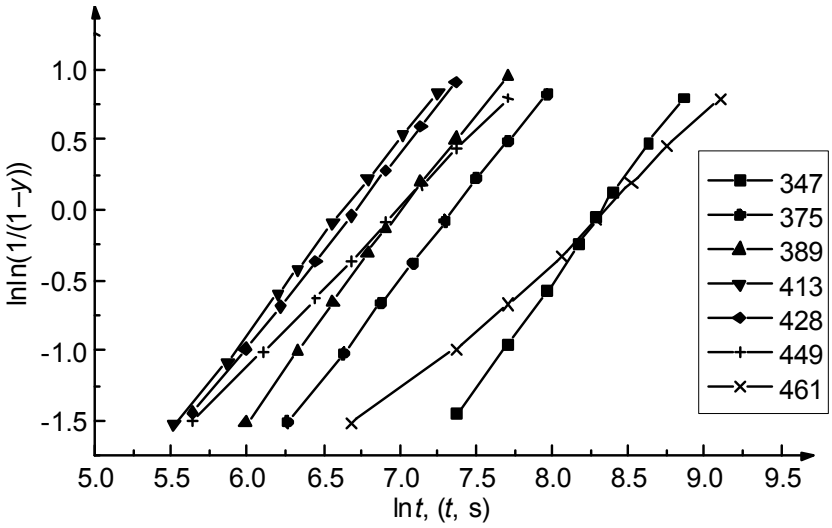

Fig. 5. Graph of the dependence of lnln[1/(1–*y*)] on ln *t*.

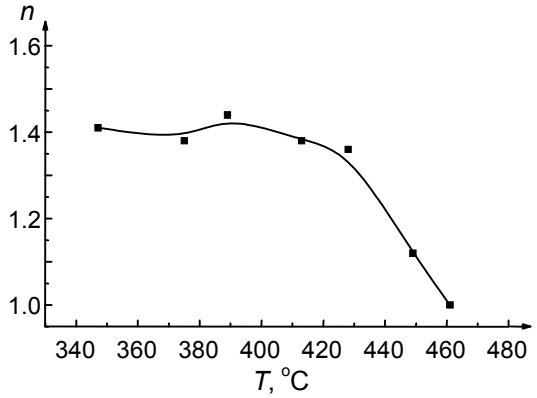

Fig. 6. Graph of the dependence of the parameter *n* on temperature *T*.

precipitation inside the grains. They proposed that the layers of the ordered phase along the grain boundaries of disordered solid solution are formed as a result of cellular decay from the boundaries, and that the lamellar precipitation inside the grains arise with participation of volume diffusion. This was indirectly confirmed by the present data with the difference that, as follows from the results presented above, these two mechanisms work in different temperature intervals and their rates strongly differ.

Thus, the ordering process in the investigated alloy takes place via two mechanisms with different values of the parameter *n*. The available experimental results make it possible to determine the activation energy with sufficient accuracy only for the low-temperature mechanism of transformation (corresponding to $n \approx 1.4$).

The activation energy *E* is determined from the Arrhenius equation

$$k = A \cdot \exp\left(-\frac{E}{R \cdot T}\right), \tag{4}$$

where *A* is a constant, *R* is the gas constant, and *T* is absolute temperature.

Taking the logarithm of Eq. (4), we obtain

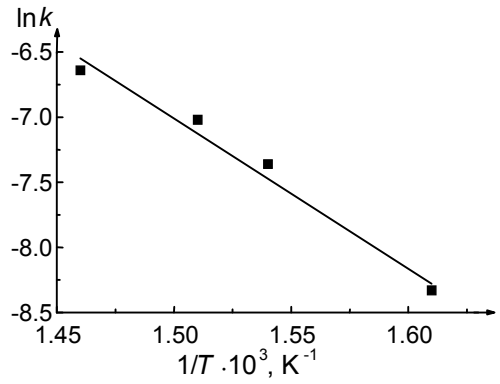

Fig. 7. Graph of the dependence of ln$k$ on 1/T.

$$\ln k = \ln A - \frac{E}{R}\frac{1}{T}. \tag{5}$$

Thus, the graph of the dependence of the logarithm of the rate constant k on the inverse temperature allows us to find the activation energy from the slope of the fitted straight line (Fig. 7).

Values of the rate constant k for different temperatures of heat treatment were calculated above (see formula (3) and Fig. 5). A straight line was fitted to the experimental points in Fig. 7 and was used in further calculations. The magnitude of the activation energy E calculated from the slope of this straight line turns out to be equal to 95 kJ/mol.

CONCLUSION

It has been established that two mechanisms of formation of an ordered structure exist in the Cu – 47 at.% Pd alloy which are determined by the temperature of heat treatment. On the basis of resistometric measurements, we calculated the activation energy E for the low-temperature mechanism of ordering, and found it to be equal to 95 kJ/mol. An examination of the literature sources allowed us to establish that the possibility of the existence of an ordering process based on two different mechanisms in Cu–Pd alloys was indicated earlier (see Reference [17]) on the basis of electron-microscope observations.

The present study once again demonstrates the need for meticulous thinking-through of an experiment with an account of all aspects of the behavior of the material. As follows from the results of the present study, an incorrect choice of techniques of sample preparation can lead to distortions of the true picture of transformation and to obtaining greatly lower values of the activation energy of the ordering process (for example, according to [12] E = 66 kJ/mol for the Cu – 48 at.% Pd alloy).

Thus, the present work has revealed the necessity of continued study of Cu–Pd alloys with the aim of examining the evolution of their structure and the formation of properties in different structural states.

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